REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*

2. REPORT TYPE
Technical Papers

3. DATES COVERED *(From - To)*

4. TITLE AND SUBTITLE

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER
2303

5e. TASK NUMBER
M2C8

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

8. PERFORMING ORGANIZATION REPORT

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Leilani Richardson
Unclassified	Unclassified	Unclassified	A		19b. TELEPHONE NUMBER *(include area code)* (661) 275-5015

62 separate items are enclosed

2303M2C8

MEMORANDUM FOR PRS (~~Contractor~~/In-House Publication)

FROM: PROI (TI) (STINFO)

24 June 1999

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-TP-FY99-0160
J.D. Presilla, J. Harper and C.W. Larson, "Kinetics of Formation of Cyclic C_6 and C_8 and B_JC_{n-J} Clusters (J = 0,1,2; n = 3-11) in Solid Argon"

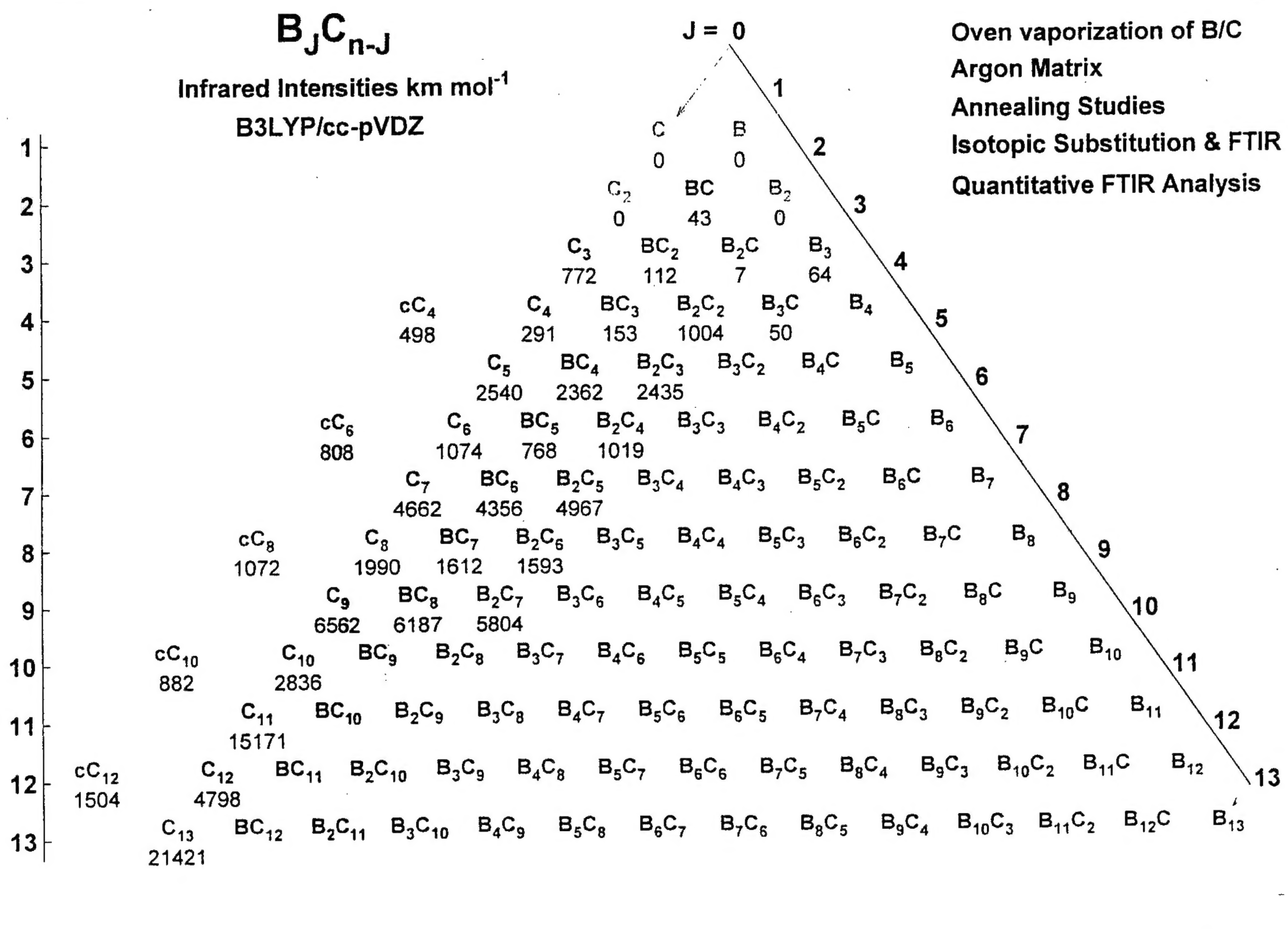
Gordon Research Conference (International) **(Statement A)**

Kinetics of formation of cyclic C_6 and cyclic C_8 and B_JC_{n-J} clusters (J = 0, 1, 2; n = 3-11) in solid argon

J. D. Presilla-Márquez, J. Harper, C. W. Larson.
Propulsion Directorate
Air Force Research Laboratory
Edwards AFB, CA 93524-7680

High Energy Density Matter (HEDM) Research Group
Pat Carrick (Chief), Jeff Sheehy (Group Leader), Greg Drake, Hi Young Yoo, Jeffrey Mills, Jerry Boatz, Jessica Harper, Karl Christe, Mario Fajardo, Michael Tinnirello, Michelle DeRose, Paul Jones, Txomin Presilla (Schafer Corporation)Peter Langhoff, Simon Tam, Suresh Suri, William Wilson,

Gordon Research Conference
Physics and Chemistry of Matrix Isolated Species
Plymouth State College
Plymouth, New Hampshire
11-16 July 1999



Goal

Production of Cryogenic HEDM with Five Mole Percent Atoms.

Objective

Characterization of species from boron atom source and subsequent condensation products

Approach

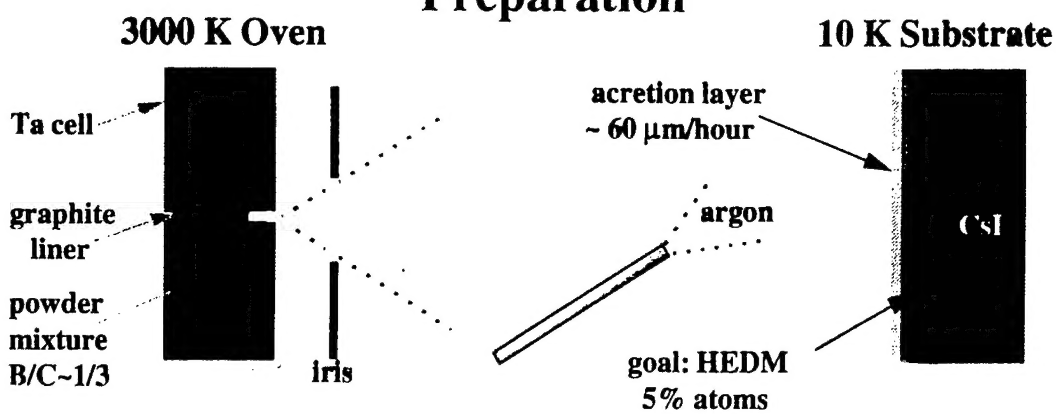
Production of HEDM by evaporation of boron with high-temperature graphite furnace and co-deposition of vapor with argon on a cold (10 K) surface

Identification and quantitative analysis of B_JC_{n-J} species ($n \geq 3$, $J = 0$ to n) by FTIR spectroscopy and *ab-initio* calculations

Quantitative measurement of distributions of B_JC_{n-J} species produced upon deposition and after annealing to a constant composition.

Absolute column densities (molecules cm^{-1}) from Beer's law: $\langle \rho_i l \rangle = 2.303\, A_{exp}/I_{theory}$

Preparation

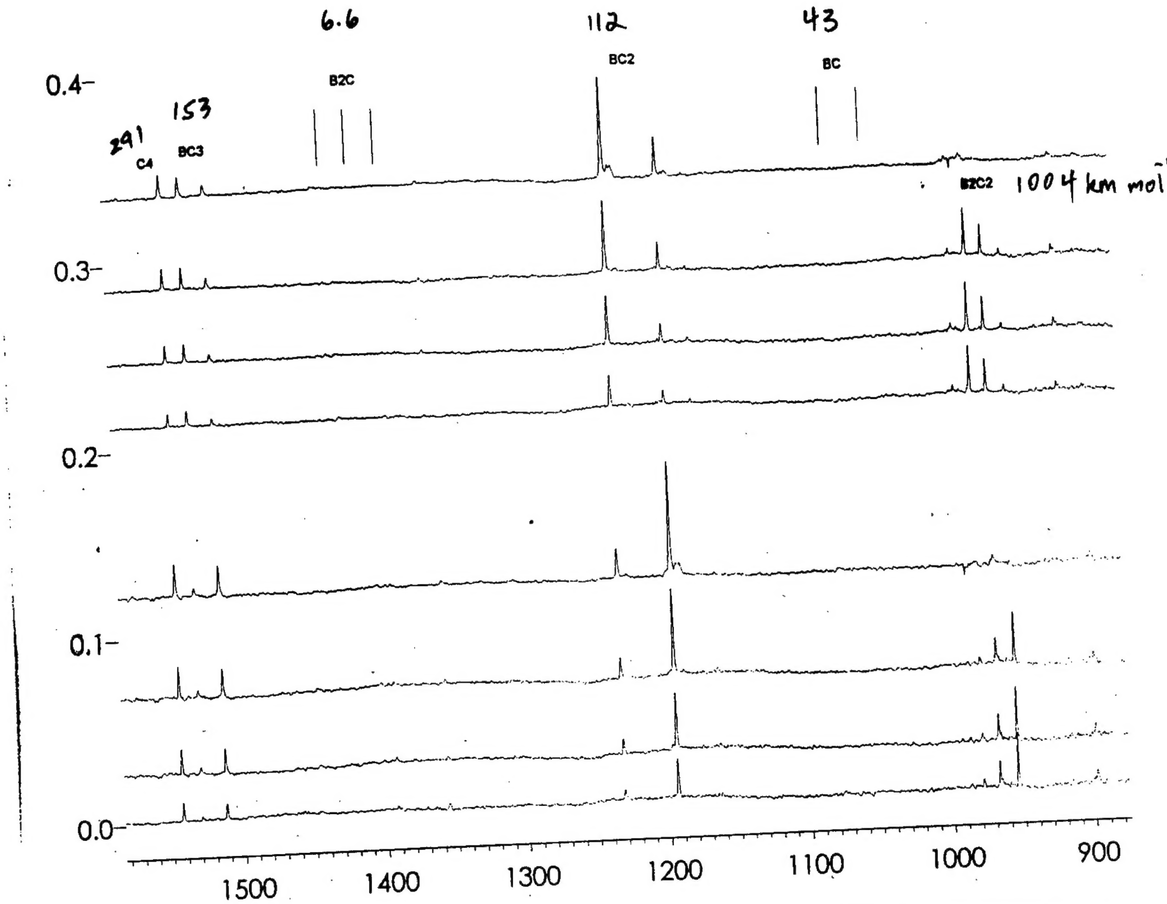


Annealing

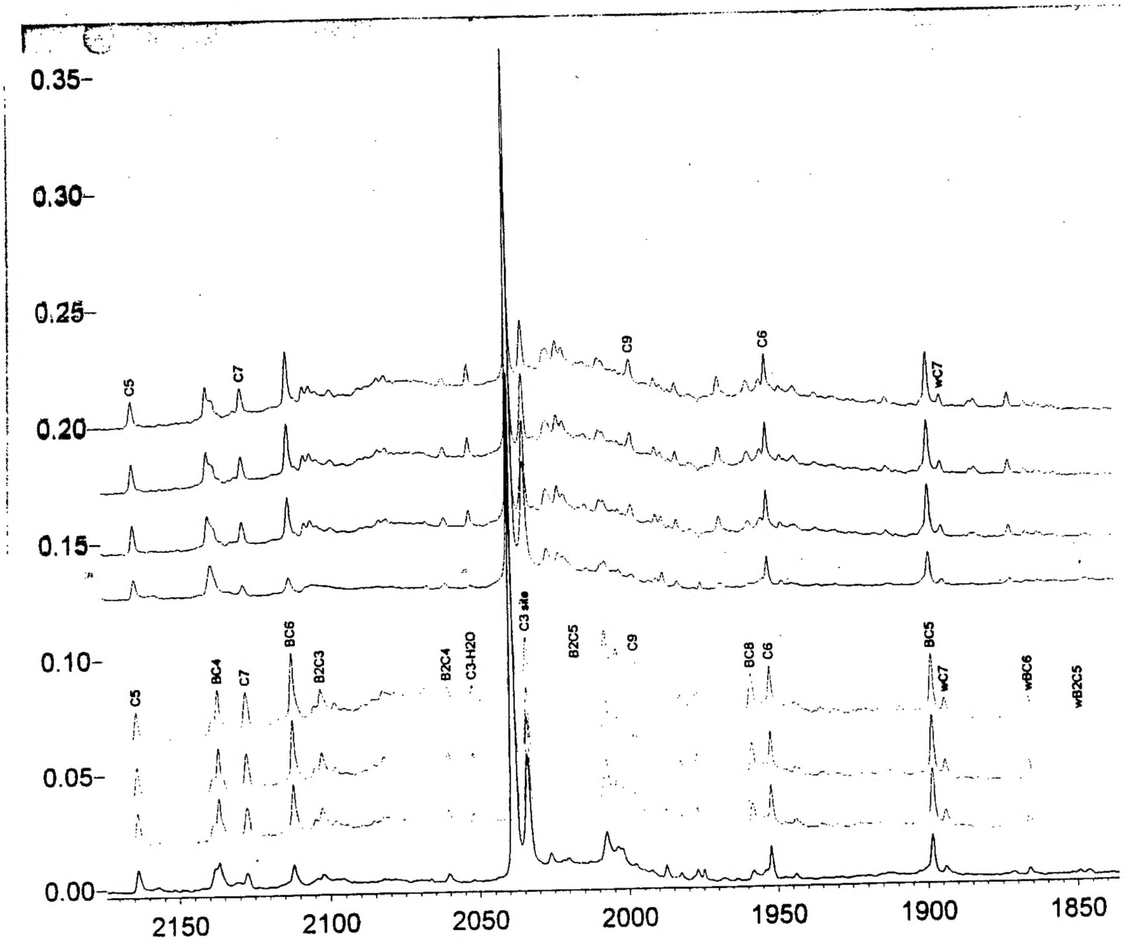
<u>a0</u> 10 K	<u>a3</u> 32.5 K, 60 s	<u>a6</u> 40.0 K, 20 s
<u>a1</u> 27.5 K, 120 s	<u>a4</u> 35.0 K, 45 s	sublimation
<u>a2</u> 30.0 K, 90 s	<u>a5</u> 37.5 K, 20 s	rate ~ 1 µm/s

Precision matched pair of matrices

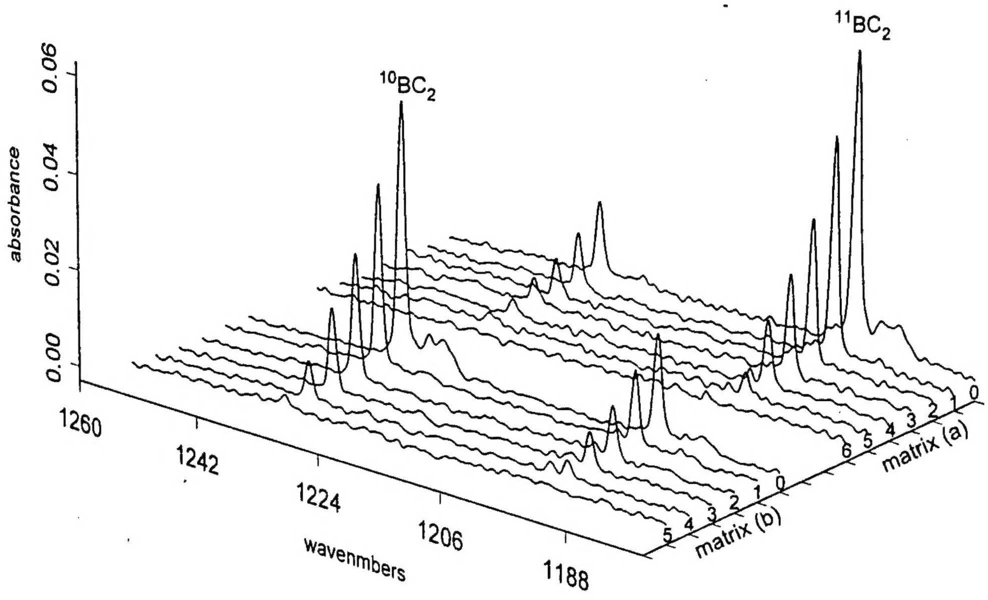
Green Matrix	$^{11}B/^{10}B = 80/20$	enhanced $^{11}B_JC_{n-J}$
Red Matrix	$^{11}B/^{10}B = 27/73$	enhanced $^{10}B_JC_{n-J}$



6.6
112
43
BC2
BC
0.4
B2C
153
291
C4
BC3
B2C2
1004 km mol^{-1}
0.3
0.2
0.1
0.0
1500
1400
1300
1200
1100
1000
900



0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
C5
C7
C9
C6
wC7
BC4
BC6
B2C3
B2C4
C3-H2O
C3 site
B2C5
BC8
BC5
wBC6
wB2C5
2150
2100
2050
2000
1950
1900
1850



BC2rg3D May 28, 1999 8:28:17 AM

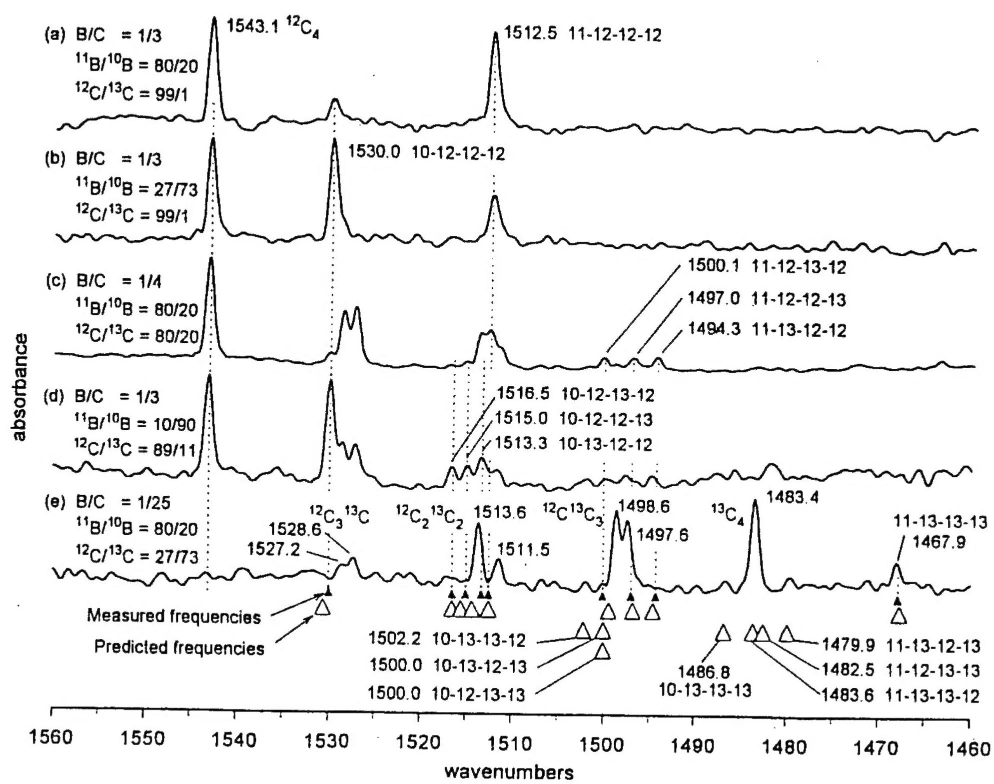
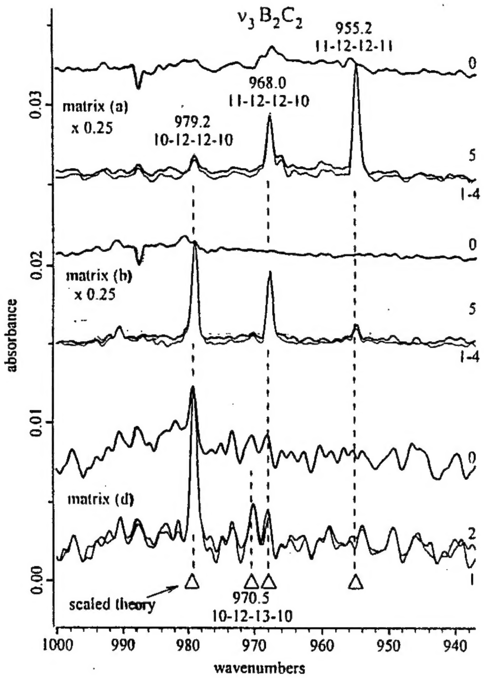
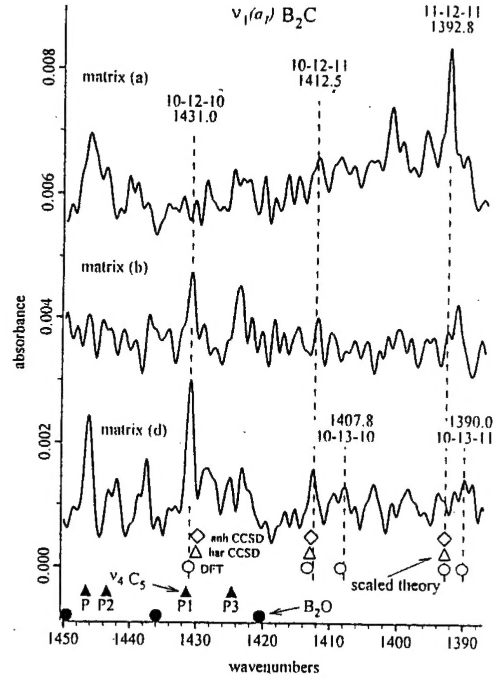


FIG. 1. FTIR spectra of the $\nu_2(\sigma)$ mode of isotopomers of linear BC_3 and the $\nu_3(\sigma_u)$ mode of isotopomers of linear C_4. The spectra were recorded at 10 K after annealing the matrices with the indicated compositions at 27.5 K for 150 s. The large open triangles at the bottom show the predicted frequencies of linear BC_3 isotopomers (as explained in the text) and small filled triangles show measured isotopomer frequencies.





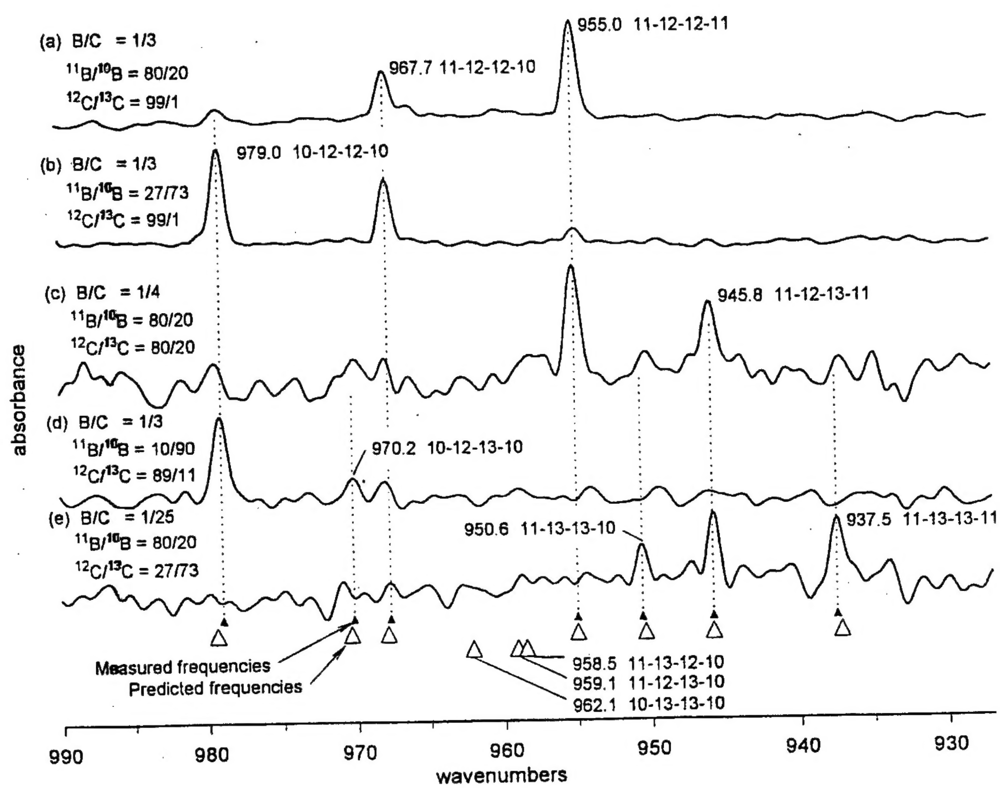


FIG. 3. FTIR spectra of the $\nu_3(\sigma_u)$ mode of isotopomers of linear BCCB. The spectra were recorded after annealing the matrices with the indicated compositions at 27.5 K for 150 s. The large open triangles at the bottom show the predicted frequencies of linear BCCB isotopomers (as explained in the text) and small filled triangles show measured isotopomer frequencies.

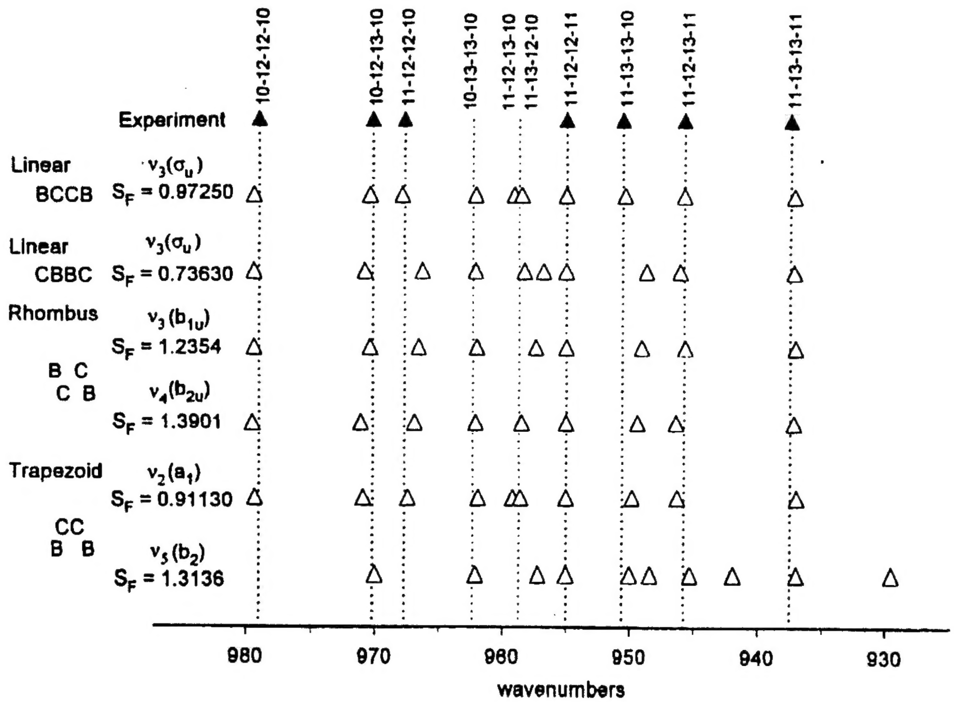
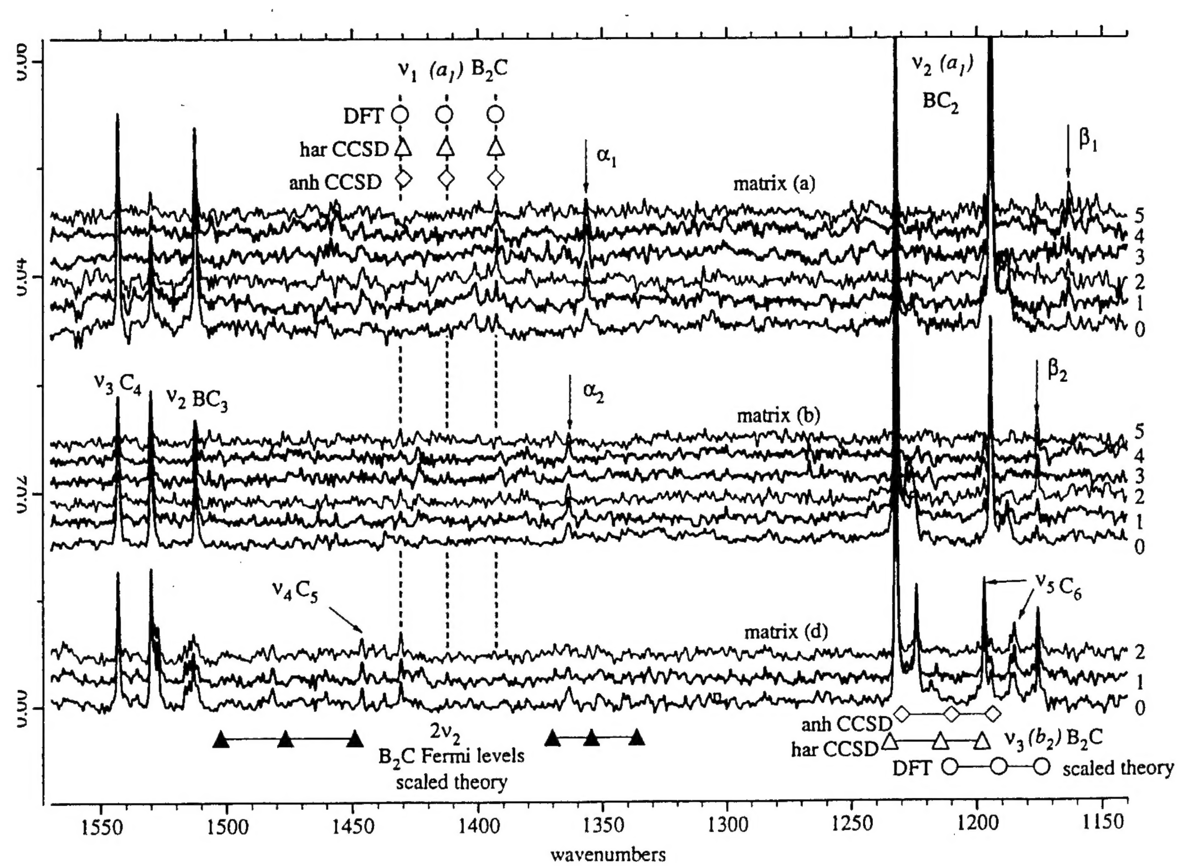
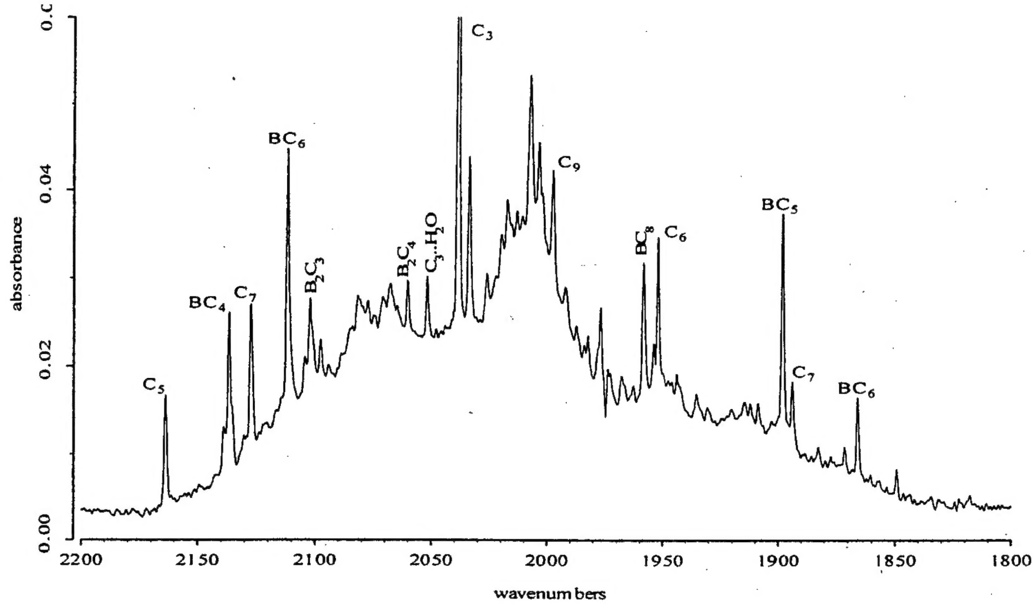


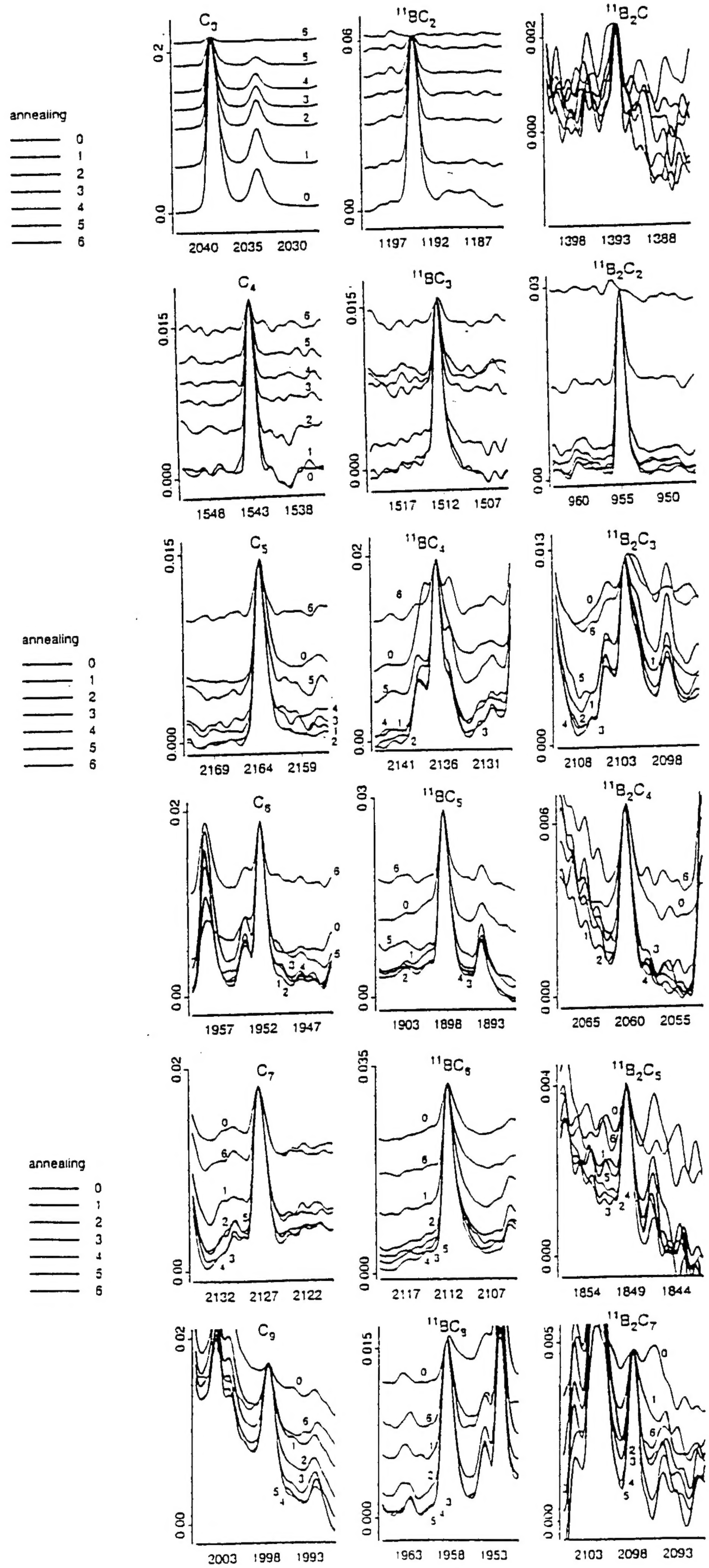
FIG. 4. Comparison of experimental isotopomer frequencies to scaled theoretical isotopomer frequencies for the most intense modes of four B_2C_2 geometries as calculated by Rittby, Ref. 5.

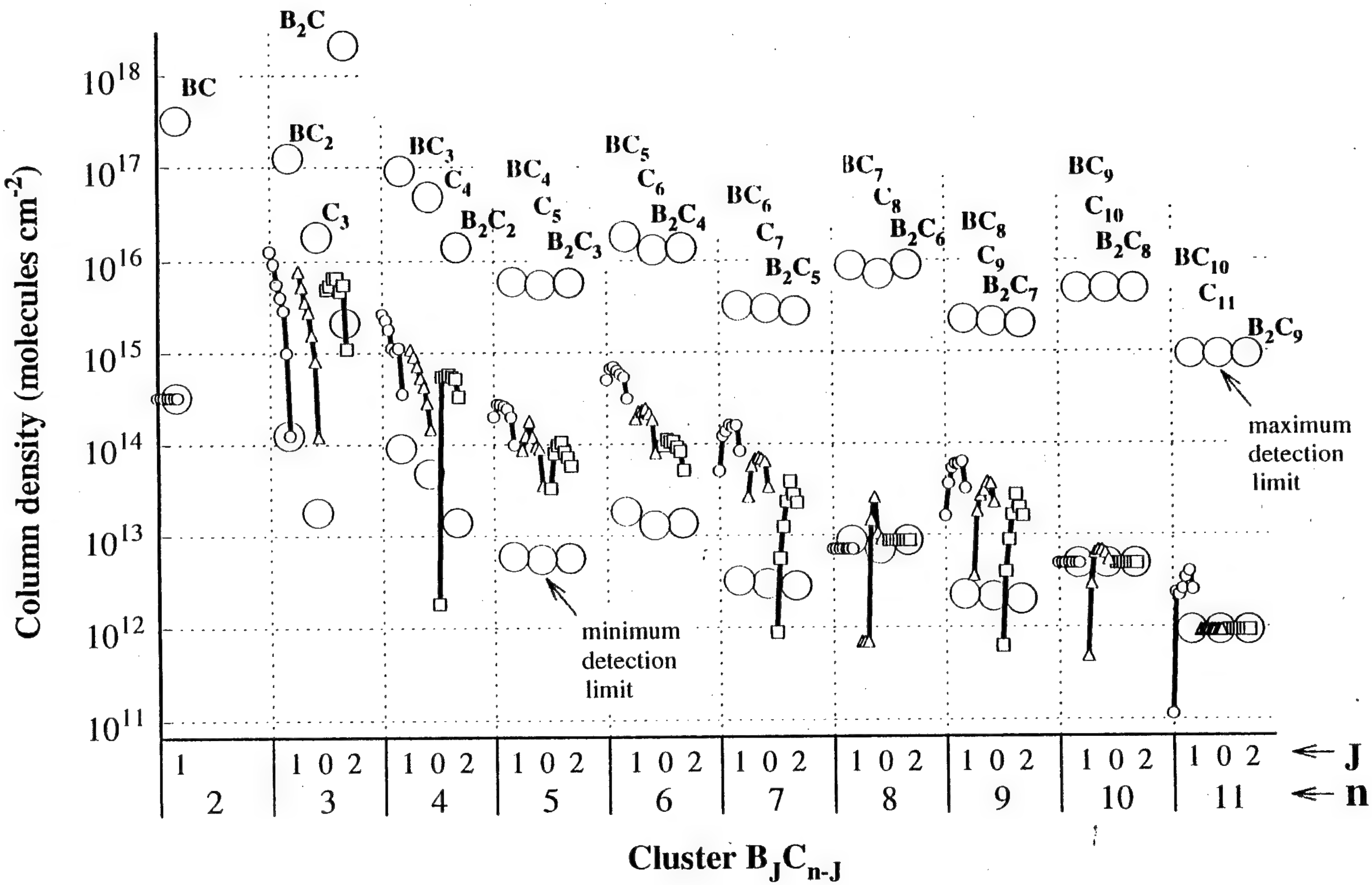




Survey spectrum of matrix containing carbon and boron at natural abundance after three annealings. All of the peaks indicated grow upon annealing except C_3. Fundamentals of BC_{n-1} for n = 5, 6, 7, and 9 are similarly red-shifted from fundamentals of linear C_n, and their experimental absorbances are all slightly greater. Two fundamentals of BC_6 are observed at 2112 and 1866 cm^{-1}, red-shifted from the two fundamentals of linear C_7.

matrix (a): $^{11}B/^{10}B = 80/20$, $^{12}C/^{13}C = 99/1$





B32mol3.axg June 2, 1999 7:21:41 AM

Results and Discussion

Linear C_3, cyclic BC_2, and cyclic B_2C, constituted about 80% of the total observable boron and carbon in the initially deposited matrix, but B_3 was not observed. If B_3 were present, its concentration fell below the detection limit of the system. The measured trimer distribution in the initially formed matrices was $\rho(C_3) : \rho(BC_2) : \rho(B_2C) : \rho(B_3) \sim 1 : 1.5 : 0.5 : < 0.05$ (upper limit).

Statistical substitution of J boron atoms into an n-atom carbon cluster produces a distribution given by $\rho(B_JC_{n-J})/\rho(C_n) = [\{n(n-1)\ldots(n-J+1)\}/J!]\ [B/C]^J$. With the experimental B/C ~ 1/3, the statistical trimer distribution is

$$\rho(C_3) : \rho(BC_2) : \rho(B_2C) : \rho(B_3) \sim 1 : 1 : 0.33 : 0.03.$$

Agreement between distributions implies trimers form by random condensation of well-mixed atoms, uninfluenced by the relative energies of the trimers, the energies of their precursors, or preferential kinetics pathways that could otherwise distort the statistics.

Linear C_3 and cyclic BC_2, disappeared entirely when the matrices were repeatedly annealed to temperatures between 25 K and 35 K, but cyclic B_2C was inert.

Linear C_4 and BC_3 (BCCC) disappeared more slowly, and linear B_2C_2 (BCCB) grew to ~ 95% of its final value during the first annealing. Once formed, B_2C_2, like B_2C, was also inert to further reaction.

The sources of B_2C_2 are from condensation of atom plus trimer ($B + BC_2$ but not $C + B_2C$) or dimer + dimer ($BC + BC$ but not $B_2 + C_2$). Although BC was not observed, the upper limit of $\rho(BC)$ is larger than $\rho(B_2C_2)$ so that BC cannot be ruled out as a source of B_2C_2.

The growth of B_2C_2 is conclusive evidence of the presence of BC and/or B in the originally deposited matrix in an amount at least as great as the growth of B_2C_2.

Linear C_5, BC_4 (BCCCC) and B_2C_3 (BCCCB)] and larger linear clusters (B_JC_{n-J}, $5 < n < 11$, $J = 0, 1, 2$), all grew upon annealing.

The sources of B_2C_3 are dimer + trimer ($BC + BC_2$ but not $B_2 + C_3$) and atom + tetramer ($B + BC_3$ but not $C + B_2C_2$).

Since $\rho(BC_2) \sim 5\rho(BC_3)$ in the initially deposited matrix, the $BC + BC_2$ source is dominant. Growth of B_2C_3 conclusively establishes the presence of BC in the matrix in an amount at least as great as the amount by which B_2C_3 grows.

Growth of BC_4 occurs primarily by $BC + C_3$ rather than $B + C_4$ or $C + BC_3$ because $\rho(C_3) \sim 10\rho(C_4)$ and $\rho(C_3) \sim 2\rho(BC_3)$. Growth of C_5 occurs by $C + C_4$ and $C_2 + C_3$, which establishes the presence of C and/or C_2 in the original matrix in an amount at least as great as C_5 growth.

Disappearance of triangular BC_2 requires breaking of one of its B-C bonds when one of its carbon atoms is attacked. The major reorganization of electronic energy involved in opening the ring appears to occur with little (< ~3 kcal mol^{-1}) or no energy barrier, which makes this small molecule a candidate for an interesting *ab-initio* study of unusual reactivity at low temperature.

Conclusions

Annealing kinetics of disappearance of C_3 and BC_2, and of appearance of B_2C, C_4, BC_3 B_2C_2, C_5, BC_4, and B_2C_3 unequivocally establishes the presence of atoms and dimers in the originally deposited matrix.

~ 80% or more of the initially deposited HEDM existed as atoms, dimers and trimers.

Molecules with two boron atoms are immune from radical attack and condensation during annealing.

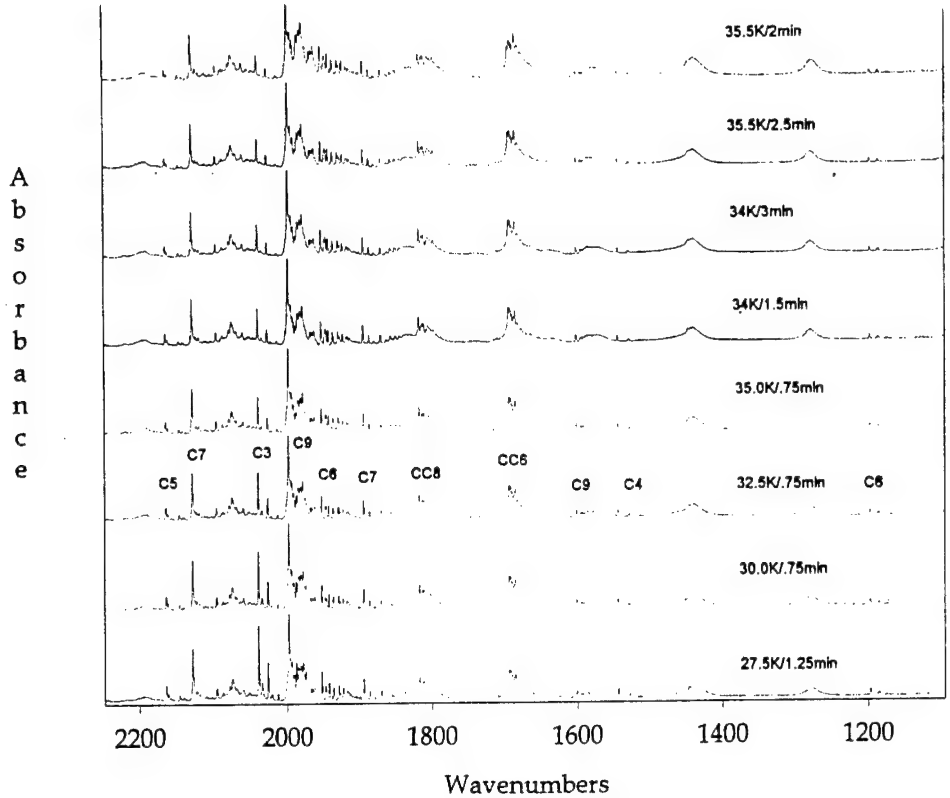
Future Work

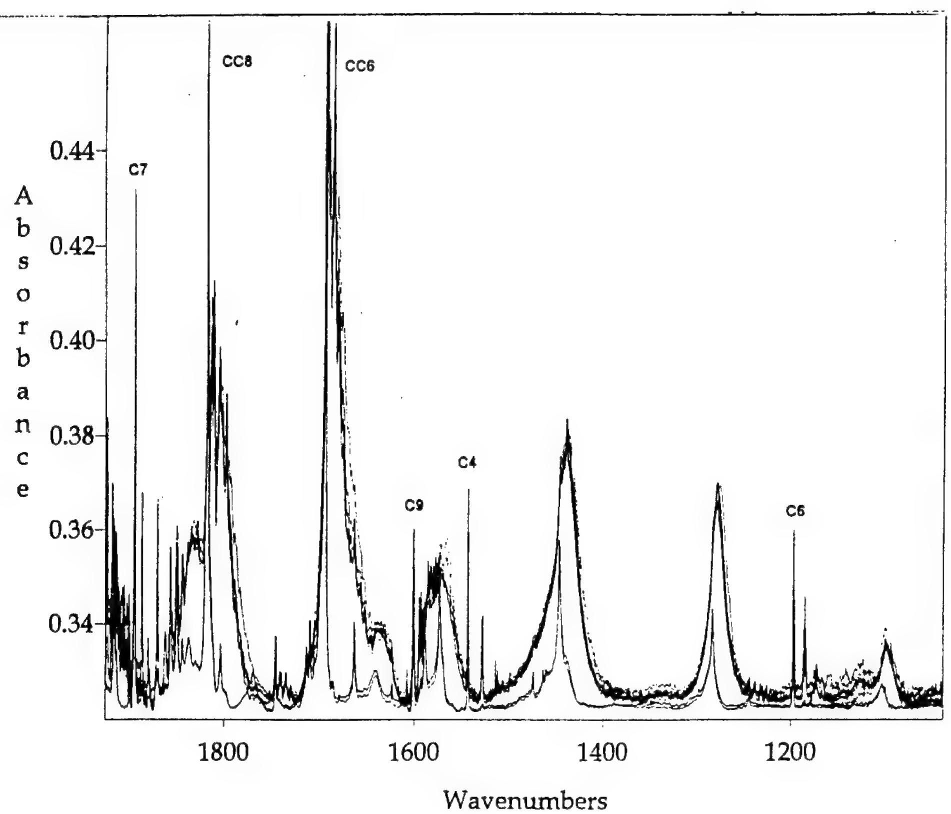
Continued development of source for production of higher flux beam of nearly pure boron atoms.

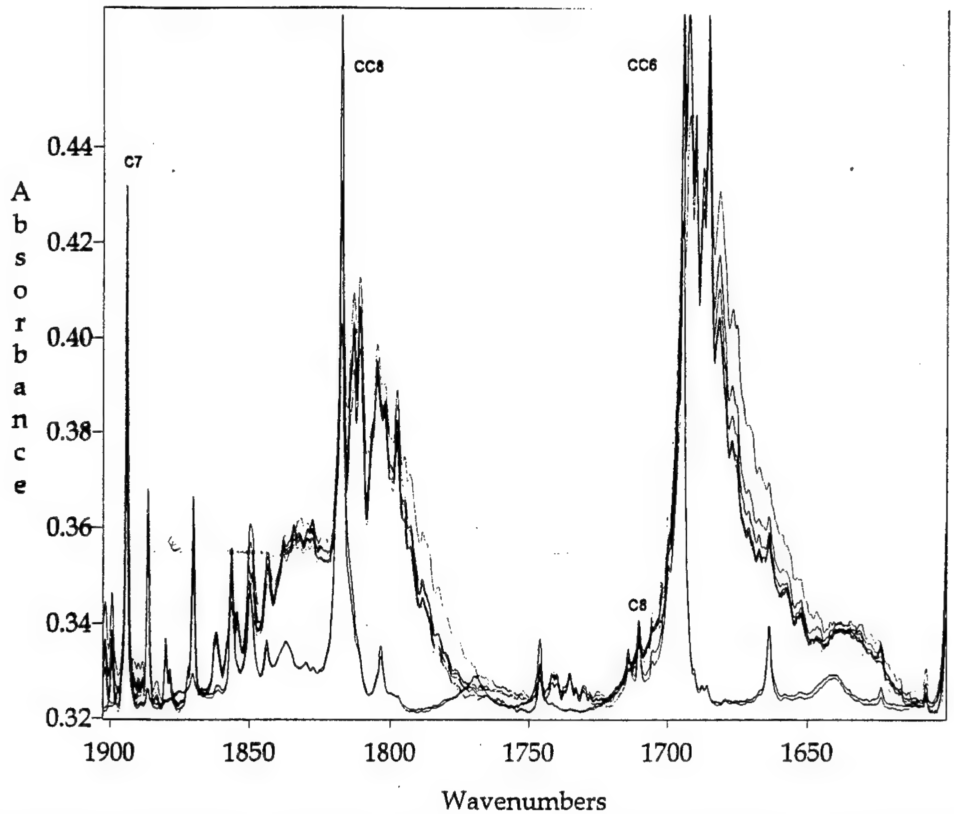
Map of "islands of stability" of pure boron HEDM; B_2 or B_3 may be the ultimate sink for atoms in the low temperature HEDM environment.

Determine reactivity of boron atoms with hydrogen during co-deposition.

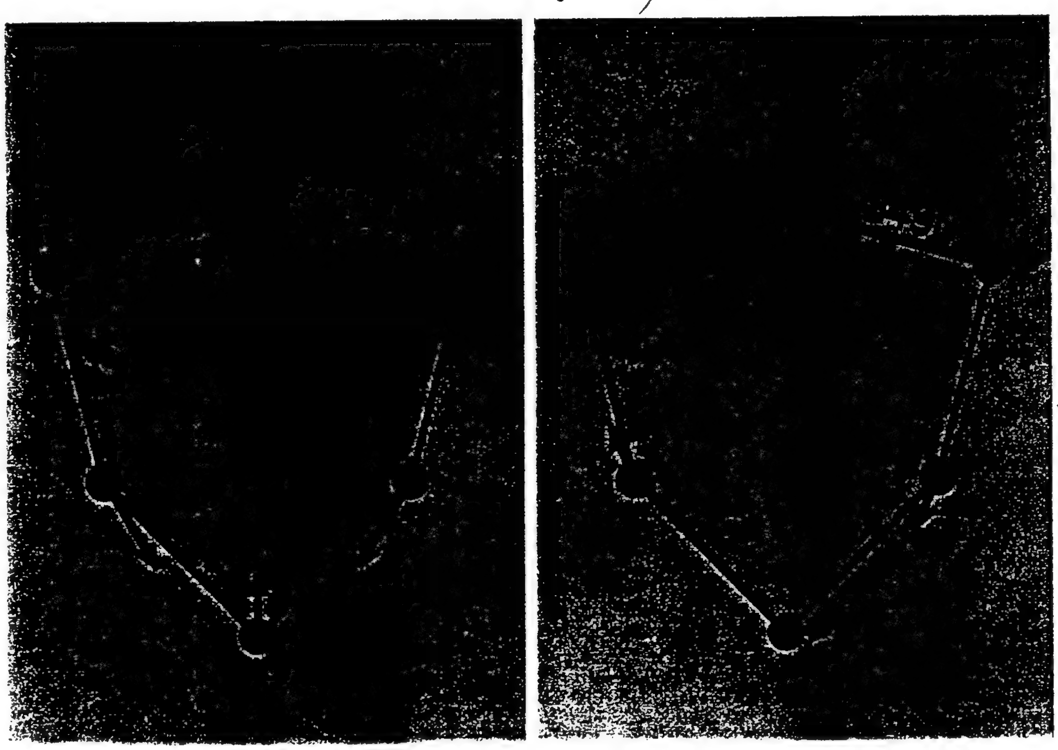
Develop rapid condensation methodology to prevent reaction of B with H_2.

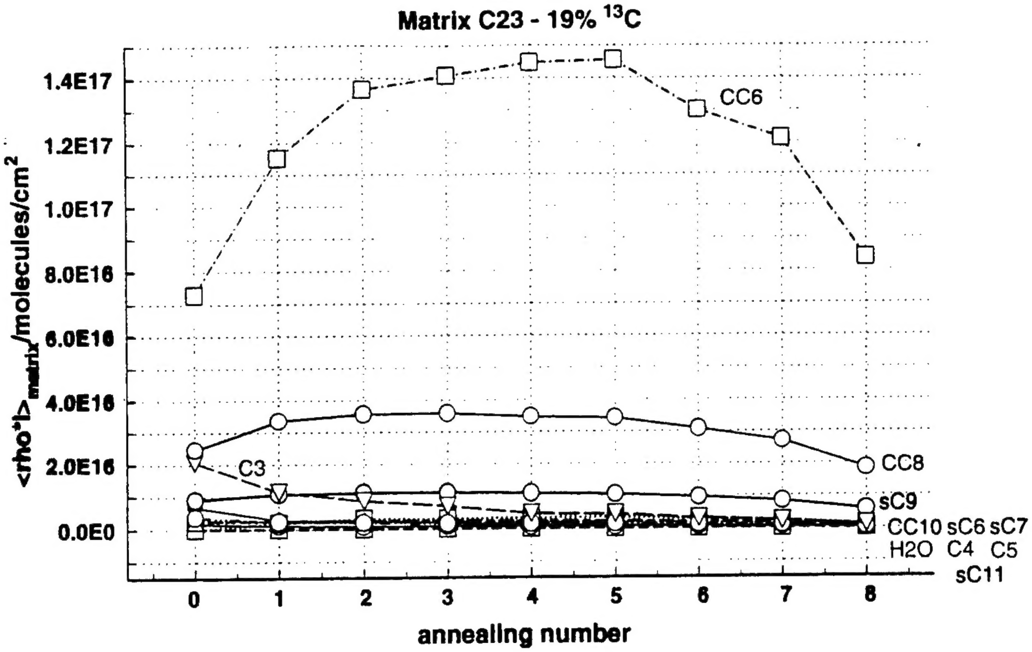

35.5K/2min
35.5K/2.5min
34K/3min
34K/1.5min
35.0K/.75min
32.5K/.75min
30.0K/.75min
27.5K/1.25min
C5
C7
C3
C9
C6
C7
CC8
CC6
C9
C4
C6
A b s o r b a n c e
2200
2000
1800
1600
1400
1200
Wavenumbers


CC8
CC6
C7
C9
C4
C6
A b s o r b a n c e
0.44
0.42
0.40
0.38
0.36
0.34
1800
1600
1400
1200
Wavenumbers

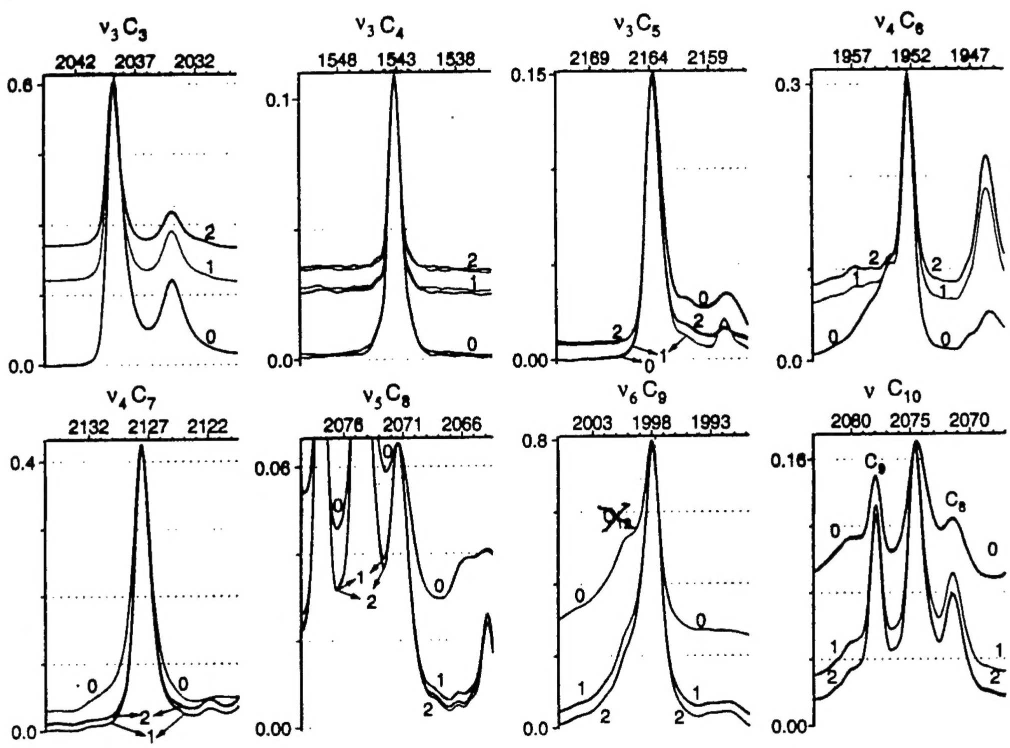

C7
CC8
CC6
C8
Absorbance
0.44
0.42
0.40
0.38
0.36
0.34
0.32
1900
1850
1800
1750
1700
1650
Wavenumbers

$\nu_4(e')$



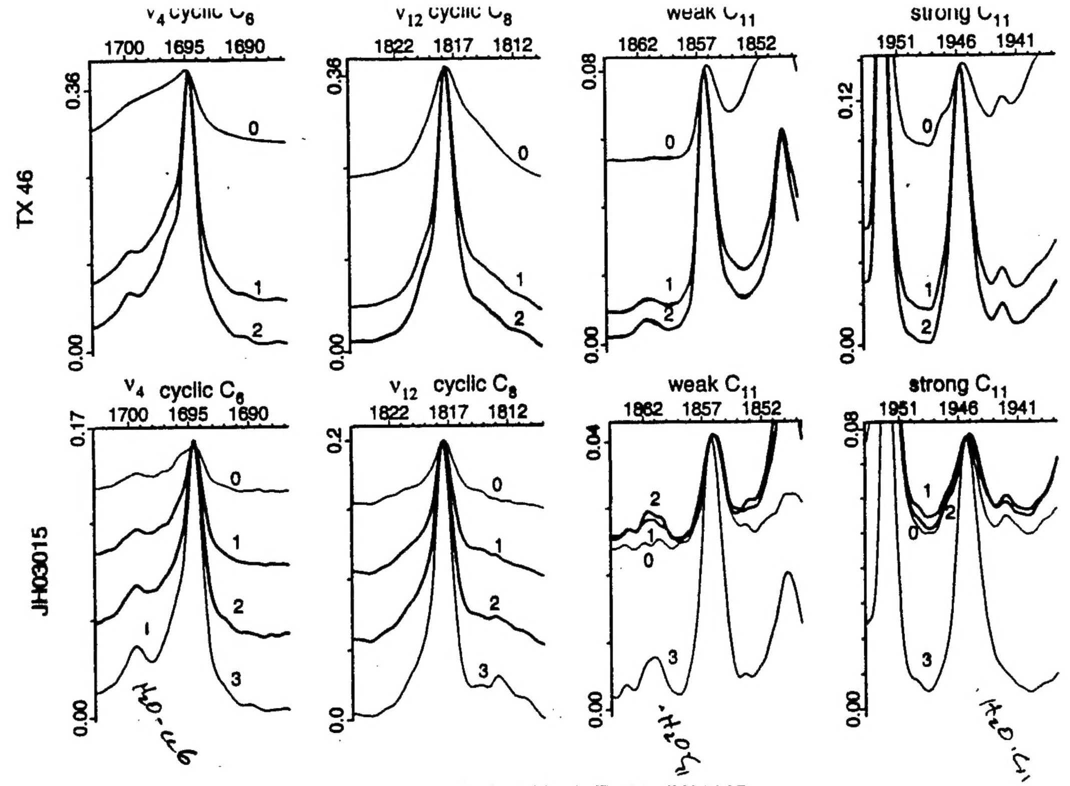


C23c2a.axg



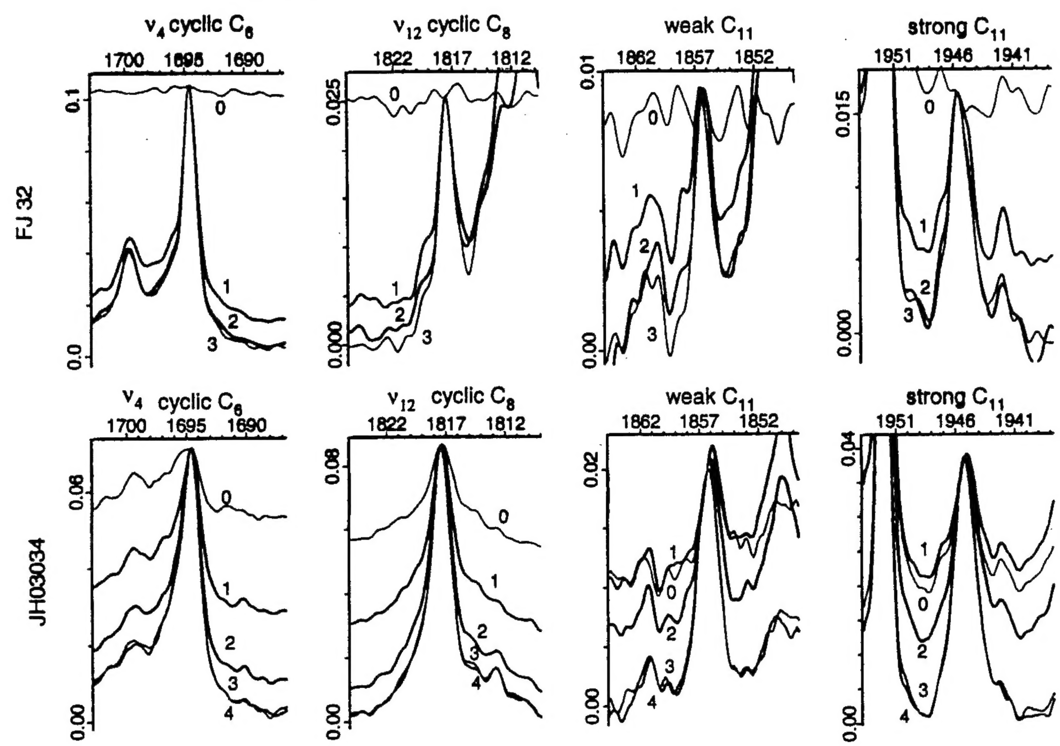
Carbon Matrix (a) - Linear C_n Clusters

MaCCn.axg May 25, 1999 5:45:39 PM



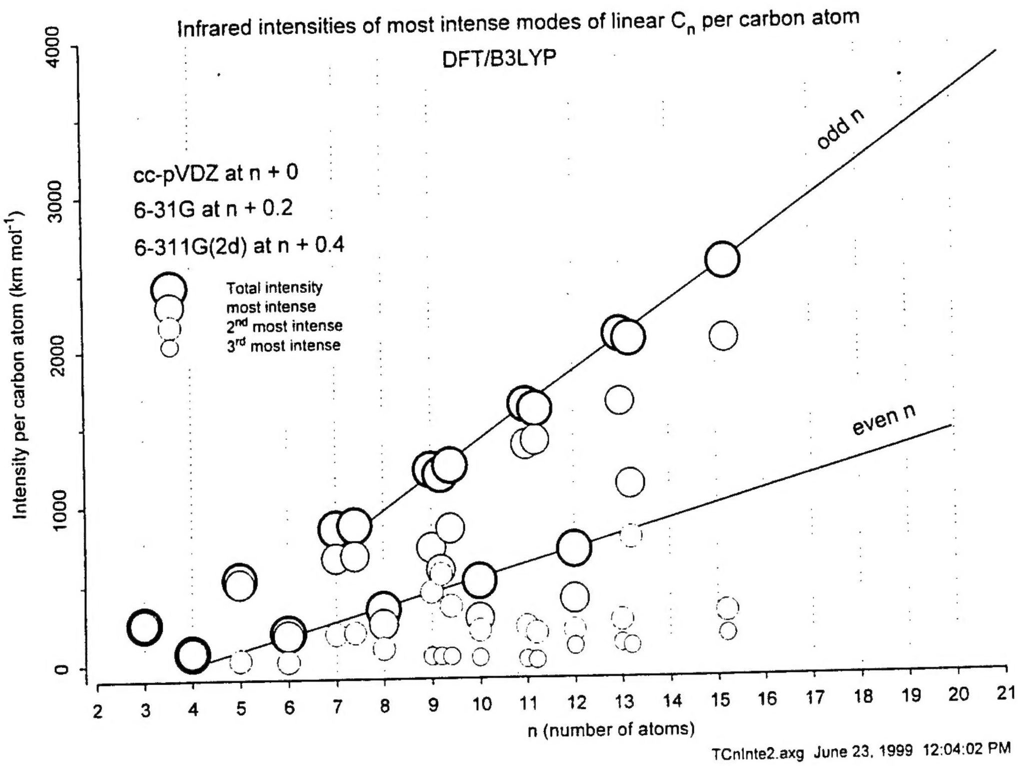
Carbon Matrix Tx 46, JH03015

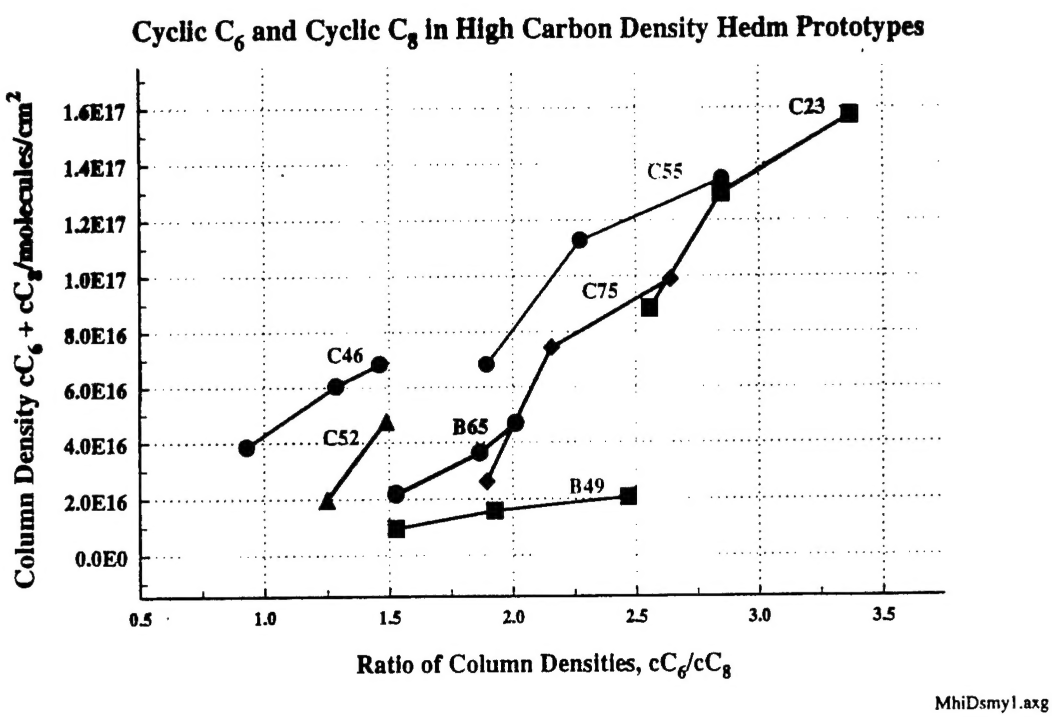
MaCCn6.axg May 25, 1999 5:25:02 PM

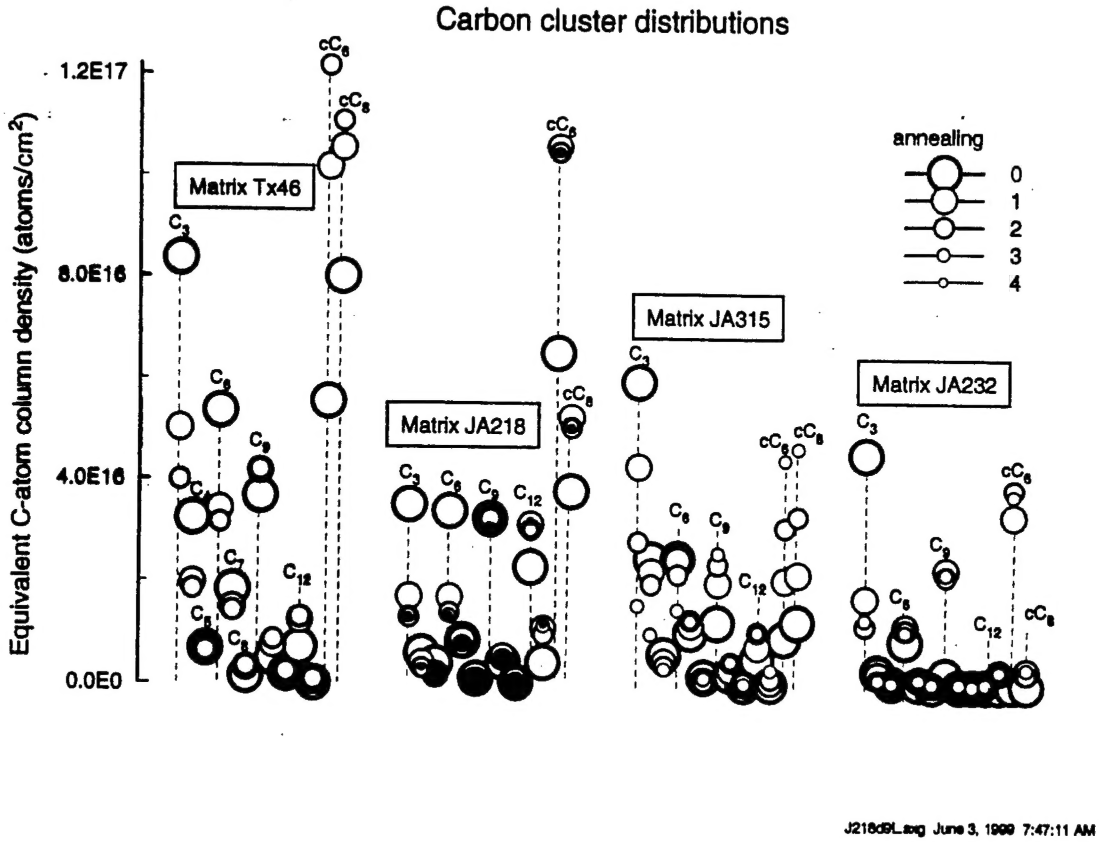


Carbon Matrix FJ 32, JA03034

MaCCn5.axg May 26, 1999 12:11:05 PM


Infrared intensities of most intense modes of linear C_n per carbon atom
DFT/B3LYP
cc-pVDZ at n + 0
6-31G at n + 0.2
6-311G(2d) at n + 0.4
Total intensity
most intense
2nd most intense
3rd most intense
odd n
even n
Intensity per carbon atom (km mol^{-1})
n (number of atoms)
TCnInte2.axg June 23, 1999 12:04:02 PM


Cyclic C_6 and Cyclic C_8 in High Carbon Density Hedm Prototypes
Column Density $cC_6 + cC_8$/molecules/cm^2
Ratio of Column Densities, cC_6/cC_8
C23
C55
C75
C46
C52
B65
B49
MhiDsmy1.axg



Conclusions from Carbon HEDM Research

Quantitative analysis - Establishes HEDM density, distribution of carbon clusters, heat of formation of HEDM. Enables tracking of growth and decay of carbon clusters - carbon bookkeeping - quantification of "invisible carbon", C-atom and C_2.

Highest density matrix (equivalent C-atom density ~ 1 mole percent in argon) contained 40% "invisible" carbon (C, C_2), determined by tracking the growth of the "visible" (measurable) carbon to a constant composition after repeated annealing. Main product of condensation is cyclic C_6.

Yields of cyclic-C_6 are a factor of two larger than the combined yield of all other clusters in the fully condensed, highest density matrices. Cyclic-C_6 is the dominant condensation product.

Knudsen oven produces ~ 80% C_3 and ~ 10% each of C_2 and C-atom (by mass).
Laval oven with $\Delta T \sim 600$ K (between graphite surface and orifice) produces ~ 5% C_3 and C_2 and ~ 90% C-atom. C-atoms production by our oven (relative to C_3) is enhanced by higher temperature, which is accompanied by higher ΔT. Langmuir evaporation produces vapor rich in atoms.

Substrate must be shielded from oven to prevent condensation during deposition.
Higher temperature oven places higher heat load on substrate, which promotes condensation.

Obtained higher density matrices by decreasing argon flux and maintaining oven flux. However, condensation was also increased.

Matrices produced with argon/5% H_2 caused nearly complete loss of C_{n+1} and C_{n+2} relative to C_{n+3}, suggesting that H_2 scavenges C-atoms efficiently during co-deposition.